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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Reaction Products of Alkoxylates and Vinyl Monomers,
Their Preparation and Their Use as Demulsifiers for
Crude Oil Emulsions

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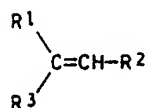
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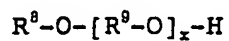
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Abstract of the Disclosure: Reaction products are prepared from predominantly hydrophilic vinyl monomers of the general formula I



I

and predominantly hydrophobic alkoxylates of the general formula II



II

and are used as demulsifiers for crude oil emulsions.

Reaction products of alkoxylates and vinyl monomers,
their preparation and their use as demulsifiers for
crude oil emulsions

5 The present invention relates to reaction products of predominantly hydrophobic alkoxylates and predominantly hydrophilic vinyl monomers, a process for their preparation and their use as mineral oil demulsifiers for rapidly dewatering crude oils.

10 In the production of crude oils, an increasing amount of water is simultaneously obtained with increasing exploitation of the deposits. Surfactants present in the crude oils emulsify the major part of the water, stable water-in-oil emulsions being formed. Salts which may lead to corrosion problems during the further processing of the crude oil in the refinery may be present
15 in solution in the emulsion water. The emulsion water must therefore be separated off or reduced below an acceptable concentration prior to transport. This is generally effected by adding mineral oil demulsifiers,
20 heating of the crude oil facilitating and accelerating the separation.

 The crude oils differ in their composition, depending on their origin. The natural emulsifiers present in the crude oils furthermore have a complicated
25 chemical composition, so that it is necessary to develop selective mineral oil demulsifiers to overcome their effect. Owing to the opening up of the new oil fields and the changed production conditions in old fields, there is a constant need for novel demulsifiers which
30 effect more rapid separation into oil and water and result in very small amounts of residual water and residual salt.

 The most frequently used demulsifiers are ethylene oxide/propylene oxide block copolymers,
35 alkoxylated alkylphenol/formaldehyde resins, alkoxylated polyamines and crosslinking products of the above basic classes with multifunctional reagents, for example

diisocyanates, dicarboxylic acids, bisglycidyl ethers and di- and trimethylolphenol.

5 Polymeric mineral oil demulsifiers are also known
(Canadian Patent 1,010,740 and DE-C1 33 38 923). Accord-
ing to this Canadian Patent, unsaturated functions which
can be subjected to free radical polymerization and which
are polymerized in a subsequent reaction with other
monomers in solution are introduced into alkoxyated
10 alcohols and alkoxyated alkylphenol/formaldehyde resins
by etherification with unsaturated diglycidyl compounds
(eg. glycidyl acrylate), by esterification with maleic
anhydride or fumaric acid or by transesterification with
acrylates or methacrylates. DE-C1 33 38 923 describes
products which are obtained by copolymerization of
15 polyoxyalkylene ethers of allyl or methallyl alcohol with
vinyl esters or acrylates or methacrylates. All of these
products have weaknesses specific to their activity or
relating to their production. For example, when glycidyl
compounds are used for introducing the unsaturated
20 functions, the formation of gels and inhomogeneities
frequently occurs during the polymerization, while
derivatives of allyl alcohol, methallyl alcohol and
maleic acid result in poor copolymerization conditions.
Furthermore, gelling and solidification reactions fre-
quently take place, particularly as a result of the use
25 of multifunctional starting alcohols in the alkoxylation.

DE 36 35 489-A1 describes copolymers of hydro-
phobic acrylates or methacrylates and hydrophilic mono-
mers. The hydrophobic esters are prepared by acid-
30 catalyzed azeotropic esterification of alkoxyates of
monohydric or polyhydric alcohols or alkylphenol/aldehyde
condensates with (meth)acrylic acid. After the copoly-
merization of the hydrophobic esters with hydrophilic
monomers, the free OH groups are converted into a form
35 which is no longer reactive and/or the catalyst acid is
neutralized with a tertiary amine. The preparation of
these products is time-consuming since the esterification

of the alkoxylate with (meth)acrylic acid requires several hours. In the esterification of alkoxylates of polyhydric alcohols, it is impossible selectively to prepare the monoester, so that, owing to the presence of multifunctional acrylates during the copolymerization with hydrophilic monomers, insoluble gels readily form.

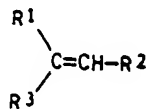
EP 0 331 323-A2 discloses demulsifiers which, however, are based on nitrogen compounds and for whose preparation long reaction times are required.

It is an object of the present invention to provide demulsifiers which permit very rapid separation into water and oil, give very small amounts of residual water, have a long shelf life and can be prepared in a simple manner and in short reaction times.

We have found that this object is achieved and that, surprisingly, products having better demulsifier activity and a longer shelf life are obtained in a short reaction time if vinyl monomers are polymerized in the presence of one or more alkoxylates without unsaturated functional groups capable of free radical polymerization having been introduced beforehand into the alkoxylates, and a condensation step is carried out after the polymerization is complete, or if the alkoxylates are condensed with polymers prepared from vinyl monomers.

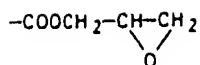
The present invention therefore relates to reaction products of alkoxylates and vinyl monomers, obtained by

a) polymerization of one or more vinyl monomers of the general formula I



I

where R^1 is hydrogen, $-\text{COOH}$, $-\text{COOC}_2\text{H}_5\text{OH}$, $-\text{COOC}_3\text{H}_7\text{OH}$, $-\text{COO}-\text{R}^4-\text{N}(\text{R}^5)_2$, $-\text{CO}-\text{NH}-\text{R}^4-\text{N}(\text{R}^5)_2$, $-\text{CONH}_2$, $-\text{CN}$, $-\text{phenyl}$, $-\text{O}-\text{CO}-\text{R}^4$, $-\text{pyridyl}$, $-\text{N}(\text{R}^5)-\text{CO}-\text{R}^6$, $-\text{COCH}_3$, $-\text{COOR}^7$, $-\text{O}-\text{R}^7$, $-\text{O}-\text{R}^7-\text{OH}$, $-\text{R}^7$, $-\text{imidazolyl}$ or



R^2 is hydrogen or -COOH , and R^1 and R^2 together may form an anhydride ring,

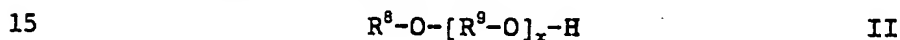
R^3 is hydrogen or CH_3 , and R^1 , R^2 and R^3 are not simultaneously hydrogen,

5 R^4 is an alkyl or alkylene group of 1 to 4 carbon atoms,

R^5 and R^6 independently of one another are each hydrogen or $\text{C}_1\text{-C}_4\text{-alkyl}$, and R^5 and R^6 together may furthermore form a 5-membered or 6-membered ring, and

10 R^7 is an alkyl, hydroxyalkyl or alkylene group of 1 to 30 carbon atoms,

in the presence of one or more alkoxyates of the general formula II



where R^8 is a radical of a monohydric or polyhydric alcohol, a phenol or alkylphenol of 1 to 30 carbon atoms or a radical of an alkylphenol/formaldehyde or alkylphenol/acetaldehyde condensate, R^9 is ethylene, propylene, 1,2-butylene or 1,4-butylene and x is from 5 to 120, and within the polyalkylene oxide chains different units $[\text{R}^9\text{-O}]$ according to the above meaning of R^9 may be present in the form of blocks or as random mixtures and x relates to the total number of all units $[\text{R}^9\text{-O}]$, and subsequent condensation

or

b) polymerization of one or more vinyl monomers of the abovementioned general formula I and
30 condensation of the resulting copolymer with one or more alkoxyates of the abovementioned general formula II,

where in each case

the vinyl monomers carry not less than 20% by weight of functional groups capable of undergoing a chemical reaction with the hydroxyl groups of the alkoxylates after the polymerization is complete,

5 the condensation is carried out so that not all hydroxyl groups are converted, and

the weight ratio of alkoxylates II to the sum of the vinyl monomers I is from 300 : 1 to 1 : 50.

Preferred reaction products are those which are
10 prepared using, as vinyl monomers of the general formula I, acrylic acid, methacrylic acid, esters or amides of these acids, vinyl ethers, acrylonitrile, vinylpyrrolidone or mixtures of these monomers. Acrylic acid
15 in an amount of from 50-100% by weight, based on the total amount of vinyl monomers, is particularly preferably used.

The alkoxylates suitable for the preparation of the novel reaction products do not contain any nitrogen.

Block copolymers which are obtained from poly-
20 hydric alcohols by reaction with propylene oxide and then with ethylene oxide are preferred, the weight ratio of propylene oxide to ethylene oxide being from 10 : 1 to 1 : 10, particularly preferably from 5 : 1 to 1 : 8.

For the preparation of the novel polymers, one or
25 more alkoxylates and one or more vinyl monomers may be used. Hydrophilic vinyl monomers are preferably used, and not more than 60% by weight of hydrophobic monomers may furthermore be present in the monomer mixture when a plurality of monomers is used. The hydrophilic monomers
30 must carry not less than 20, preferably 40, particularly preferably 60, % by weight of functional groups capable of undergoing a chemical reaction with the hydroxyl groups of the alkoxylates after polymerization is complete.

35 Examples of suitable vinyl monomers are acrylic acid, methacrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, isobutyl (meth)acrylate, lauryl acrylate,

hydroxyethyl (meth)acrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylamide, glycidyl methacrylate, vinylformamide, vinyl acetate, vinyl propionate, styrene, isobutene, trimethylpentene, allyl alcohol, vinyl methyl ether, vinyl 4-hydroxybutyl ether, vinylimidazole, vinylpyrrolidone, maleic acid and fumaric acid. Acrylic acid or monomer mixtures which contain not less than 50% by weight of acrylic acid are particularly preferred.

The weight ratio of alkoxylate to the sum of the vinyl monomers is from 300 : 1 to 1 : 50, preferably from 100 : 1 to 1 : 10, particularly preferably from 30 : 1 to 1 : 1.

A) Preparation of the alkoxylates (DE 36 35 489-A1, pages 5, 32-67)

The alkoxylated alcohols are prepared in a known manner by reacting the monofunctional or polyfunctional alcohol with an alkoxide or with a mixture of a plurality of alkoxides or block by block with a plurality of alkoxides with the aid of basic catalysts at from 80 to 160°C. Examples of suitable alcohols are ethanol, butanol, isopropanol, tallow fatty alcohol, stearyl alcohol, alkylphenols of the general formula



where R is, for example, C_9H_{19} , CH_3 , $CH(CH_3)_2$, $C(CH_3)_3$ or C_6H_{17} , ethylene glycol, bisphenol A, glycerol, trimethylolpropane, pentaerythritol, sorbitol, polyglycerol or the alkylphenol/formaldehyde or acetaldehyde condensates described below.

Preferred alkoxides are ethylene oxide, propylene oxide and 1,2-butylene oxide or mixtures thereof.

The reaction conditions vary depending on the type and amount of the alkoxides used. In general, the reaction temperature is from 80 to 160°C and the amount of basic catalysts varies from 0.25 to 5%, potassium hydroxide and sodium hydroxide being preferred.

Depending on the consistency of the starting alcohol or of the end product, an inert solvent which does not influence the reaction may be added for dilution. Xylene is preferred.

5 The ratio of alcohol to alkoxide(s) may vary greatly but is advantageously from 1 : 120 to 1 : 5. Alkoxyated alkylphenol/formaldehyde or acetaldehyde condensates

10 The alkylphenol/formaldehyde or acetaldehyde resins used as alcohols for the alkoxylation are prepared in a conventional manner by reacting the aldehyde with the alkylphenol in a ratio of from 2 : 1 to 1 : 2, preferably 1 : 1.05, with base or acid catalysis, preferably acid catalysis, at from 80 to 250°C, with the aid of
15 a high boiling solvent for complete azeotropic removal of the resulting water of reaction. For example, nonylphenol, tert-butylphenol or octylphenol is used as the alkylphenol, while preferably used aldehydes are formaldehyde and acetaldehyde. In general, an alkylsulfonic
20 acid or alkylbenzenesulfonic acid, for example dodecylbenzenesulfonic acid, is used as the catalyst, in amounts of from 0.2 to 2%, preferably from 0.2 to 0.5%.

 At the beginning of the reaction, the temperature is kept at from 90 to 120°C until the major part of the
25 water of reaction has been distilled off. Thereafter, the mixture is heated to the boiling point of the solvent to ensure complete conversion, and residual amounts of water are removed azeotropically. The molecules contain on average from 4 to 12, preferably from 5 to 9, aromatic
30 nuclei.

 The condensates thus obtained are alkoxyated as stated above.

 The pure alkoxyates have, as a rule, very little or no activity as mineral oil demulsifiers. Highly
35 effective products are obtained only as a result of the copolymerization with the vinyl monomers and the subsequent condensation step or condensation of the

alkoxylates with the polymers prepared from vinyl monomers.

B) Preparation of the novel polymers

5 The preparation of the novel polymers can be carried out in principle by two methods:

- a) by effecting the polymerization of the vinyl monomers in the presence of the alkoxylate and effecting condensation step after polymerization is complete, or
- 10 b) by polymerizing the vinyl monomers separately from the alkoxylate and not adding the alkoxylate until before the condensation step.

15 Process a) is, as a rule, preferred. In this process, some of the vinyl monomers are grafted onto the alkoxylate. The degree of grafting depends to a very great extent on the polymerization conditions and on the type of alkoxylate as the grafting base. The presence of graft copolymer has proven advantageous in many cases.

20 Process b) is preferably chosen when vinyl monomers which do not dissolve in the alkoxylate or in solvents in which the alkoxylate dissolves are to be polymerized or when, even before the polymerization is complete, the monomers would undergo with the alkoxylate the chemical reaction similar to that when, for example, 25 maleic anhydride is used as a comonomer.

The polymerization of the vinyl monomers according to variant a) or b) is carried out by the known batchwise or continuous methods of free radical polymerization, such as mass, suspension, precipitation or 30 solution polymerization, and initiation with conventional free radical donors, such as acetylcyclohexanesulfonyl peroxide, diacetyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, tert-butyl perneodecanoate, 2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile), tert-butyl perpivalate, tert-butyl per-2-ethylhexanoate, tert-butyl permaleate, 2,2'- 35 azobisisobutyronitrile, bis-(tert-butylperoxy)cyclo-

hexane, tert-butyl peroxyisopropyl carbonate, tert-butyl peracetate, dicumyl peroxide, di-tert-amyl peroxide, di-tert-butyl peroxide, p-menthane hydroperoxide, cumyl hydroperoxide or tert-butyl hydroperoxide and mixtures with one another. In general, these initiators are used in amounts of from 0.1 to 20, preferably from 0.2 to 15, % by weight, based on the monomers.

The polymerization is carried out as a rule at from 40 to 200°C, preferably from 60 to 150°C, in the course of from 0.5 to 10, preferably from 1 to 6, particularly preferably from 2 to 3, hours, and advantageously under superatmospheric pressure when solvents having boiling points below the polymerization temperature are used. The polymerization is advantageously carried out in the absence of air, ie. when it is not possible to work under boiling conditions, for example under nitrogen or carbon dioxide, since oxygen inhibits the polymerization. The reaction can be accelerated by the presence of redox coinitiators, such as benzoin, dimethylaniline, ascorbic acid and soluble organic complexes of chromium. The amounts usually used are from 0.1 to 2,000, preferably from 0.1 to 1,000, ppm by weight.

To obtain low molecular weight copolymers, it is often advantageous to work in the presence of regulators. Examples of suitable regulators are allyl alcohols, such as but-1-en-3-ol, organic mercapto compounds, such as 2-mercaptoethanol, 2-mercaptopropanol, mercaptoacetic acid, mercaptopropionic acid, tert-butyl mercaptan, n-butyl mercaptan, n-octyl mercaptan, n-dodecyl mercaptan and tert-dodecyl mercaptan, which are generally used in amounts of from 0.1 to 10% by weight.

Apparatuses suitable for the polymerization are, for example, conventional stirred kettles having, for example, anchor, paddle or impeller stirrers or multi-stage impulse countercurrent agitators and, for continuous preparation, stirred kettle cascades, tubular

reactors and static mixers.

The simplest polymerization method is mass polymerization. Here, the monomers are polymerized in the presence of an initiator and in the absence of solvents. Advantageously, all monomers are mixed to give the desired composition, and a small portion, for example from about 5 to 10%, is initially taken in the reactor together with the alkoxylate (according to process a)) and heated to the desired polymerization temperature with stirring, and the remaining monomer mixture and the initiator and, if required, coiniciator and regulator are metered in uniformly in the course of from 1 to 10, preferably from 2 to 5, hours. It is advantageous to meter in the initiator and the coiniciator separately in the form of solutions in a small amount of suitable solvent. The condensation step can then be carried out in the melt. The end product can then be added to the crude oil emulsion directly as solidified melt or after being taken up in a suitable solvent.

A further simple method for the preparation of the novel polymers is solution polymerization. It is carried out in solvents in which the monomers and the resulting copolymers are soluble. All solvents which meet this precondition and which do not undergo any reaction with the monomers are suitable for this purpose.

Examples are toluene, xylene, ethylbenzene, cumene, high boiling mixture of aromatics, such as Solvesso® 100, 150 and 200, aliphatic and cycloaliphatic hydrocarbons, eg. n-hexane, cyclohexane, methylcyclohexane, n-octane, isooctane, liquid paraffins, Shellsol® TD, T and K and acetone, cyclohexanone, tetrahydrofuran and dioxane, tetrahydrofuran and dioxane being particularly suitable for obtaining low molecular weight copolymers.

Since the demulsifiers for crude oil emulsions are surfactants which should be soluble in the continuous phase (oil phase) of the crude oil emulsion, it is

advantageous to choose, for the polymerization, a solvent which is compatible with the emulsion, so that the demulsifier solution can be added directly to the emulsion. Solution polymerization is the preferred method of preparation for the novel copolymers.

5 In carrying out the solution polymerization, it is advantageous initially to take the solvent, the alkoxylate and some of the monomer mixture (for example from about 5 to 20%) and to meter in the remainder of the monomer mixture with the initiator and, if required, 10 coinitiator, regulator and solvent. The monomers may also be metered in individually at different rates. This is advisable in the case of monomers having greatly different reactivities and if particularly uniform 15 distribution of the less reactive monomer is desired. The less reactive monomer is metered in more rapidly and the more reactive monomer more slowly. It is also possible initially to take the total amount of the monomer, preferably of the the less reactive monomer, and 20 to meter in only the more reactive one. Finally, it is also possible initially to take the total monomers, the alkoxylate and the solvent and to meter in only the initiator and, if required, coinitiator and regulator (batchwise procedure). When this procedure is carried 25 out on a larger scale, however, problems may be encountered with heat removal, so that this procedure should be used only at low concentrations of the monomers to be polymerized. The concentrations of said monomers are from 5 to 80, preferably from 10 to 50, % by weight.

30 C) The condensation step

In the condensation step, some of the free hydroxyl groups of the alkoxylate are reacted with some of the reactive groups of the polymer of the vinyl monomers (for example acrylic acid or esters thereof). 35 This results in bridging, so that very effective demulsifiers are formed. The composition of the alkoxylate and of the vinyl monomers and the reaction conditions

must be chosen so that completely oil-soluble end products are obtained. Hence, all of the hydroxyl groups of the alkoxylate must not be converted in the condensation step since insoluble products would form; instead, low conversions are generally sufficient to obtain the desired effect.

The preferred reaction in the condensation step is esterification.

The condensation is carried out as a rule at from 80 to 250°C, preferably from 100 to 200°C, particularly preferably at from 120 to 180°C, in the course of from 0.5 to 10, preferably from 1 to 8, particularly preferably from 2 to 6, hours, in the melt or in solution. If the boiling point of the solvent is below the desired condensation temperature, the condensation is carried out under superatmospheric pressure.

To carry out the condensation step, the reaction mixture, consisting of alkoxylate and polymer of vinyl monomers and, if required, solvent, is brought to the desired temperature. In some cases, it is advantageous to remove the low molecular weight reaction products (for example water or low molecular weight alcohols) from the reaction vessel. This may be effected, for example, by passing in an inert gas over the polymer melt or by using an entraining agent. If it is intended to remove, for example, water from the reaction mixture, suitable entraining agents are the conventional organic solvents which form an azeotropic mixture with water, in particular xylene or toluene. The condensation can be accelerated by adding catalysts, in particular acidic catalysts, such as sulfuric acid, p-toluenesulfonic acid, dodecylbenzenesulfonic acid, hydrochloric acid or acidic ion exchangers. If a catalyst acid is added, it must be neutralized after the end of the condensation step. All basic compounds are in principle suitable for this purpose. However, amines such as triethylamine, ethylhexylamine, tributylamine, morpholine, piperidine or

ethanolamine are preferably used. Not less than the stoichiometric amount of base required for neutralizing the catalyst acid is added. However, it is also possible to add a larger amount of base. In this case, the remaining acidic groups introduced by the vinyl monomers, especially carboxyl groups which originate from the acrylic acid, are also partially or completely neutralized. The activity of the demulsifiers can be adapted to the crude oil emulsions by the correct choice of the base and of the degree of neutralization.

The novel polymers possess both better activity and a longer shelf life compared with the demulsifiers described in German Laid-Open Application DOS 3,365,489, without it being necessary to convert the free hydroxyl groups of the alkoxylate into ether, ester or urethane groups. Such a conversion can also be carried out in the case of the novel polymers but has no further advantages with regard to activity or stability.

D) Modification of the polymer of B) and C) (optional)

For increasing the activity and tailoring to the particular crude oil to be treated, subsequent modification of the copolymers obtained under B) and C) may be useful. The following modification of the product may be carried out, depending on the comonomers used in the copolymerization:

1) Mixing with an alkoxyated alcohol or a mixture of a plurality of alkoxyated alcohols obtained as described under A) or with other copolymers of B) and C) in a ratio of from 10 : 90 to 90 : 10, preferably from 50 : 50 to 80 : 20.

Better activities can also be achieved by adding cosurfactants to the copolymers in amounts of from 5 to 30% by weight. Such cosurfactants may be, for example, dodecyl bisulfate, alkylbenzenesulfonates or alkylnaphthalenesulfonates.

2) The molecular weight can be increased by subsequent crosslinking with polyfunctional crosslinking

reagents which react with reactive groups in the copolymer. Depending on the type of crosslinking agent, crosslinking is carried out using from 0.1 to 10, preferably from 1 to 4, % by weight of polyfunctional components at from 80 to 140°C. Depending on the comonomers used, suitable polyfunctional crosslinking agents are, for example, bisglycidyl ethers (preferably bisglycidyl ether of bisphenol A), polyfunctional alcohols (eg. sorbitol or ethylene glycol), diisocyanates (eg. toluene diisocyanate) and comparable compounds which react with reactive centers in the copolymer.

3) Subsequent oxyalkylation with an alkoxide or a mixture of a plurality of alkoxides or block by block with different alkoxides. The copolymers of B) and C) are reacted with the alkoxide(s) in the presence of basic catalysts (preferably sodium hydroxide or potassium hydroxide) in amounts of from 0.5 to 5% by weight at from 100 to 150°C. Preferably used alkoxides are ethylene oxide, propylene oxide or 1,2-butylene oxide, the ratio of copolymer to alkoxide varying from 5 : 95 to 95 : 5.

4) Quaternization of N-containing copolymers with known quaternizing agents, such as dimethyl sulfate or methyl iodide, at from 50 to 120°C. Complete or partial quaternization of the amine functions present may be effected.

Modification of copolymer C) is not restricted to the use of only one method of modification. Instead, any modifications according to 1) to 4) may be carried out in succession.

The novel polymers may also be used as a mixture with other demulsifiers, for example those based on alkoxylated amines.

The K values (according to H. Fikentscher, Cellulosechemie 13 (1932), 58-64 and 71-74, determined in 2% (w/v) solution in xylene) of the novel polymers are from 10 to 50, preferably from 10 to 40, particularly preferably from 13 to 30.

The novel additives are added to the mineral oil emulsions in amounts of from 0.5 to 1,000, preferably from 1 to 200, ppm.

5 The Examples which follow illustrate the invention.

The alkoxylates can be prepared, for example, as described in DE 36 35 489-A1. In the Examples, the meanings are as follows:

- 10 A1: Block copolymer of 1 mol of propylene glycol reacted with (on average) 30.0 mol of propylene oxide and then with (on average) 10.4 mol of ethylene oxide.
- A2: Block copolymer of 1 mol of propylene glycol reacted with (on average) 47.4 mol of propylene oxide and then with (on average) 20.0 mol of ethylene oxide
- 15 (= Example a3 from German Laid-Open Application DOS 3,365,489).
- A3: Block copolymer of 1 mol of propylene glycol reacted with (on average) 20.5 mol of propylene oxide and then with (on average) 11.6 mol of ethylene oxide.
- 20 A4: Block copolymer of 1 mol of trimethylolpropane reacted with (on average) 80.0 mol of propylene oxide and then with (on average) 30.3 mol of ethylene oxide (= Example a15 from German Laid-Open Application DOS 3,365,489).
- 25 A5: Polytetrahydrofuran having a molecular weight of about 2,000 g/mol.

Preparation of the novel polymers

EXAMPLE 1

30 In a reactor provided with a stirrer, a heating means and a feed apparatus, a solution of 152 g of alkoxylate A1 in 126 g of xylene was heated to 70°C in a gentle stream of nitrogen, and a solution of 30 g of acrylic acid in 30 g of xylene and simultaneously a solution of 0.6 g of AIBN (azobisisobutyronitrile) in

35 26 g of xylene were metered in uniformly in the course of 2 hours. Heating was then carried out for a further hour at 70°C. A whitish turbid polymer solution of about 50%

strength and having a K value of 20.3 was obtained.

0.8 g of p-toluenesulfonic acid was added to this polymer solution and the mixture was refluxed (140°C) for two hours. It was then cooled to 40°C and 0.7 g of morpholine was added.

EXAMPLE 2

The procedure was as in Example 1, except that alkoxyate A2 was used. A milky transparent polymer solution of about 50% strength by weight and having a K value of 21.5 was obtained. The condensation was carried out similarly to Example 1.

EXAMPLE 3

The procedure was as in Example 1, except that alkoxyate A3 was used. A translucent polymer solution of about 50% strength by weight and having a K value of 19.8 was obtained. The condensation was carried out after the addition of p-toluenesulfonic acid by distilling off water azeotropically in the course of two hours. The catalyst acid was neutralized by adding an equimolar amount of triethanolamine.

EXAMPLE 4

The procedure was as in Example 1, except that polyether A5 was employed instead of alkoxyate A1, and 54 g of acrylic acid and 1.3 g of AIBN were used for the polymerization. A whitish turbid polymer solution of about 50% strength by weight and having a K value of 24.2 was obtained. The condensation and neutralization were carried out similarly to Example 1.

EXAMPLE 5

In a reactor according to Example 1, 190 g of alkoxyate A4, 159 g of xylene, 27 g of acrylic acid and 1 g of p-toluenesulfonic acid were initially taken and were heated to 70°C while stirring and passing through nitrogen. Thereafter, 1.5 g of AIBN in 60 g of xylene were metered in uniformly in the course of 2 hours, heating was continued for one hour at 70°C and refluxing

5 was carried out for a further 3 hours. After the mixture had cooled to room temperature, 1.5 g of tri-n-butylamine were added. A brownish, transparent polymer solution of about 50% strength and having a K value of 19.2 was obtained.

EXAMPLE 6

10 In a reactor according to Example 1, 100 g of alkoxylate A4, 14.2 g of acrylic acid and 0.53 g of p-toluenesulfonic acid were heated to 65°C while stirring and passing through nitrogen, and 100 mg of AIBN were added. After a few minutes, the temperature increased to 77°C. After the exothermic reaction had died down, the mixture was kept at 70°C and a further 200 mg of AIBN were added. The mixture was kept at 70°C for a further hour 15 and then heated at 135-140°C for 1 hour. The viscous polymer melt was cooled to 50°C and then taken up in the same amount of Solvesso® 150 (high boiling mixture of aromatics) and 2 g of morpholine.

EXAMPLE 7

20 The procedure was similar to that of Example 1, but with alkoxylate A4 and Solvesso® 150 as a solvent. For condensation, the mixture was heated at 160°C for 2 hours.

25 In Examples 8 to 21, the procedures were similar to those of the Examples shown in the last column of Table 1.

TABLE 1

Exam- ple	Alkox- ylate	Parts	Monomers		Parts of		Temp. °C	Initiator		Regulator		Similar to Example
			1.	2.	monomers	Type		%	Type	%		
											1	
5												
	A4	190	AA	-	13.4	-	70	AIBN	5.5	-	-	5
	A4	190	AA	-	53.6	-	70	AIBN	2.0	-	-	1
10	A4	190	AA	-	80.4	-	70	AIBN	2.0	-	-	1
	A4	190	AA	-	40.2	-	70	AIBN	2.0	ME	2.0	1
	A4	190	AA	-	53.6	-	90	TBPO	1.3	-	-	3
	A4	190	AA	-	26.8	-	110	TBPO	2.0	-	-	1
	A4	342	AA	EA	57.9	14.5	70	AIBN	2.0	-	-	1
	A4	190	AA	HEA	36.2	4.0	70	AIBN	2.0	-	-	1
	A4	342	AA	VP	57.9	14.5	70	AIBN	2.0	-	-	1
15	A4	190	AA	LA	36.2	4.0	70	AIBN	2.0	-	-	1
	A4	190	AA	AN	36.2	4.0	70	AIBN	2.0	-	-	1
	A4	190	AA	V4-OH	36.2	4.0	70	AIBN	2.0	-	-	1
	A4	190	AA	MAA	36.2	4.0	70	AIBN	2.0	-	-	1
20	A4	342	AA	S	65.2	7.2	70	AIBN	2.0	-	-	1

*) % by weight, based on the vinyl monomers

	AA	Acrylic acid
	EA	Ethyl acrylate
	VP	Vinylpyrrolidone
25	LA	Lauryl acrylate (mixture of n-dodecyl and n-tetradecyl acrylate)
	AN	Acrylonitrile
	V4-OH	4-Hydroxybutyl vinyl ether
	MAA	Methacrylic acid
30	S	Styrene

EXAMPLE 22

In a reactor according to Example 1, 65 g of alkoxyate A4, 81 g of xylene, 0.35 g of p-toluene-sulfonic acid and 32.2 g of a 50.5% strength by weight aqueous solution of a copolymer of 50 parts of acrylic acid and 50 parts of maleic acid, having a molecular weight of 3,000 g/mol, were heated to the boil and about 16.5 g of water were separated off azeotropically in the course of 2 hours. The mixture was diluted to 35% by weight with xylene, and water was separated off for a

further hour. A clear, yellowish solution was obtained by dilution with xylene to about 10% by weight.

COMPARATIVE EXAMPLE (EXAMPLE B18 from DE 36 35 489-A1)

1. Preparation of the ester (Example A15)

5 In a reactor according to Example 1, 426.3 g of alkoxylate A4, 5.53 g of acrylic acid, 5.53 g of p-toluenesulfonic acid, 85 mg of hydroquinone monomethyl ether and 187.6 g of xylene were heated to the boil for three hours, the water of reaction then being removed by
10 azeotropic distillation. A clear, brown solution was obtained. The acid number was 3.9 mg of KOH/g.

2. Copolymerization with acrylic acid (Example B18)

In a reactor according to Example 1, 223.3 g of the ester from 1., 23.95 g of acrylic acid, 113 mg of
15 AIBN and 113.2 g of xylene were heated to 80°C while passing through nitrogen and were kept at this temperature for three hours. Thereafter, heating was continued for two hours at 110°C, the mixture was cooled to 30°C and 1.96 g of tri-n-butylamine were added. A yellowish-
20 brown, clear, viscous polymer solution having a K value of 28.5 was obtained.

The novel polymers were tested using various crude oil emulsions. For this purpose, the corresponding amount of demulsifier was added to the emulsion while
25 stirring, and removal of water was monitored as a function of time in a measuring cylinder. The temperature required for optimum demulsification was achieved by placing the measuring cylinder in a thermostated water bath. The numerical values shown in Tables 2 and 3
30 correspond to the percentage of water removed, based on the total water content of the emulsion (= 100%).

Crude oil emulsion I

Origin:	Rühlernmoor/Georgsdorf
Water content:	47% by volume
35 Demulsification temperature:	50°C

TABLE 2

	Product from Example	Dose (ppm)	Amount of water removed in % after						
			minutes				hours		
			10	20	30	45	1	2	4
5	1	8	0	0	0	7	24	49	70
	2	5	2	21	69	94	96	99	100
	5	6	2	10	28	74	88	98	100
	6	8	0	2	5	13	45	71	89
10	12	10	0	2	18	67	97	99	100
	14	3	2	10	20	88	94	97	100
	17	5	2	7	20	68	91	96	99
	Comp. Example	10	0	0	0	0	3	5	8

Crude oil emulsion II

15 Origin: Adorf/Scherhorn
 Water content: 51% by volume
 Demulsification temperature: 50°C

TABLE 3

	Product from Example	Dose (ppm)	Amount of water removed in % after						
			minutes				hours		
			10	20	30	45	1	2	4
20	2	20	8	21	38	63	94	99	100
	5	25	15	20	28	35	59	88	99
25	7	15	8	12	21	31	50	69	100
	10	10	4	6	18	25	52	92	98
	11	10	4	12	21	33	63	94	100
	14	15	4	21	38	67	92	99	100
	18	10	9	29	56	78	91	98	99
30	Comp. Example	25	0	0	0	5	9	14	21

The values shown in Tables 2 and 3 indicate the good activity of the novel polymers as demulsifiers for crude oil emulsions. The low dose and the short demulsification time are typical. The comparative

product has substantially poorer activity in a similar dose.

We claim:-

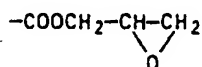
1. A reaction product of alkoxyates and vinyl monomers, obtained by

a) polymerization of one or more vinyl monomers of the formula I



where R^1 is hydrogen, $-\text{COOH}$, $-\text{COOC}_2\text{H}_5\text{OH}$, $-\text{COOC}_3\text{H}_7\text{OH}$, $-\text{COO}-\text{R}^4-\text{N}(\text{R}^5)_2$, $-\text{CO}-\text{NH}-\text{R}^4-\text{N}(\text{R}^5)_2$, $-\text{CONH}_2$, $-\text{CN}$, $-\text{phenyl}$, $-\text{O}-\text{CO}-\text{R}^4$, $-\text{pyridyl}$, $-\text{N}-\text{CO}-\text{R}^6$, $-\text{COCH}_3$, $-\text{COOR}^7$, $-\text{O}-\text{R}^7$,
 R^5

$-\text{O}-\text{R}^7-\text{OH}$, $-\text{R}^7$, $-\text{imidazolyl}$ or



R^2 is hydrogen or $-\text{COOH}$, and R^1 and R^2 together may form an anhydride ring,

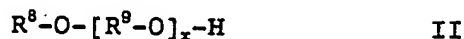
R^3 is hydrogen or CH_3 , and R^1 , R^2 and R^3 are not simultaneously hydrogen,

R^4 is an alkyl or alkylene group of 1 to 4 carbon atoms,

R^5 and R^6 independently of one another are each hydrogen or C_1-C_4 -alkyl, and R^5 and R^6 together may furthermore form a 5-membered or 6-membered ring, and

R^7 is an alkyl, hydroxyalkyl or alkylene group of 1 to 30 carbon atoms,

in the presence of one or more alkoxyates of the formula II



where R^8 is a radical of a monohydric or polyhydric alcohol, a phenol or alkylphenol of 1 to 30 carbon atoms or a radical of an alkylphenol/formaldehyde or alkylphenol/acetaldehyde condensate, R^9 is ethylene, propylene, 1,2-butylene or 1,4-butylene and x is from 5 to 120, and within the polyalkylene oxide

chains different units $[R^9-O]$ according to the above meaning of R^9 may be present in the form of blocks or as random mixtures and x relates to the total number of all units $[R^9-O]$,
5 and subsequent condensation

or

b) polymerization of one or more vinyl monomers of the abovementioned formula I and
condensation of the resulting copolymer with one or
10 more alkoxylates of the abovementioned formula II,
where in each case

the vinyl monomers carry not less than 20% by weight of functional groups capable of undergoing a chemical reaction with the hydroxyl groups of the alkoxylates after the polymerization is complete,
15 the condensation is carried out so that not all hydroxyl groups are converted, and
the weight ratio of alkoxylates II to the sum of the vinyl monomers I is from 300 : 1 to 1 : 50.

20 2. A reaction product as claimed in claim 1, wherein the vinyl monomer of the formula I is acrylic acid, methacrylic acid, an ester or amide of acrylic acid or methacrylic acid, vinyl ether, acrylonitrile, vinylpyrrolidone or a mixture of these monomers.

25 3. A reaction product as claimed in claim 1, wherein the vinyl monomer of the formula I contains from 50 to 100% by weight of acrylic acid.

4. A reaction product as claimed in claim 1, wherein, in the formula II, R^9 is ethylene and propylene.

30 5. A mixture containing a reaction product as claimed in claim 1 and, if required, surfactants, solvents or further demulsifiers.

6. Process for the preparation of a reaction product as claimed in claim 1, comprising

35 a) polymerization of one or more vinyl monomers of the formula I as claimed in claim 1 or 2 or 3 in the presence of one or more alkoxylates of the formula

II as claimed in claim 1 or 4 and subsequent condensation

or

- 5 b) polymerization of one or more vinyl monomers of the formula I as claimed in claim 1 or 2 or 3 and condensation of the resulting copolymer with one or more alkoxylates of the formula II as claimed in claim 1 or 4,

where in each case

- 10 the vinyl monomers carry not less than 20% by weight of functional groups capable of undergoing a chemical reaction with the hydroxyl groups of the alkoxylates after the polymerization is complete, the condensation is carried out so that not all
15 hydroxyl groups are converted, and the weight ratio of alkoxylates II to the sum of the vinyl monomers I is from 300 : 1 to 1 : 50.

- 20 7. A method for using a reaction product as claimed in claim 1, wherein the reaction product is employed as a demulsifier in crude oil emulsions.

8. A method for using a mixture as claimed in claim 5, wherein the mixture is employed as a demulsifier in crude oil emulsions.